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MeV Si ion modifications on the thermoelectric generators from Si/Si + Ge superlattice nano-layered films

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A B S T R A C T

The performance of thermoelectric materials and devices is characterized by a dimensionless figure of merit, $ZT = S^2 \sigma T/K$, where, S and σ denote, respectively, the Seebeck coefficient and electrical conductivity, T is the absolute temperature in Kelvin and K represents the thermal conductivity. The figure of merit may be improved by means of raising either S or σ or by lowering K. In our laboratory, we have fabricated and characterized the performance of a large variety of thermoelectric generators (TEG). Two TEG groups comprised of 50 and 100 alternating layers of Si/Si + Ge multi-nanolayered superlattice films have been fabricated and thoroughly characterized. Ion beam assisted deposition (IBAD) was utilized to assemble the alternating sandwiched layers, resulting in total thickness of 300 nm and 317 nm for 50 and 100 layer devices, respectively. Rutherford Backscattering Spectroscopy (RBS) was employed in order to monitor the precise quantity of Si and Ge utilized in the construction of specific multilayer thin films. The material layers were subsequently impregnated with quantum dots and/or quantum clusters, in order to concurrently reduce the cross plane thermal conductivity, increase the cross plane Seebeck coefficient and raise the cross plane electrical conductivity. The quantum dots/clusters were implanted via the 5 MeV Si ion bombardment which was performed using a Pelletron high energy ion beam accelerator. We have achieved remarkable results for the thermoelectric and optical properties of the Si/Si + Ge multilayer thin film TEG systems. We have demonstrated that with optimal setting of the 5 MeV Si ion beam bombardment fluences, one can fabricate TEG systems with figures of merits substantially higher than the values previously reported.

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1. Introduction

Thermoelectric devices utilizing the Seebeck and the Peltier effects have gained considerable attention in recent years. They offer viable solutions to an assortment of technological challenges ranging from spot cooling of high density-high speed electronic systems, to harvesting generated heat and conversion to electrical energy for storage, to remote power generation in space, satellite applications, etc. These solid state devices can be fabricated economically and offer excellent durability and operational reliability owing to lack of any moving components. However, to date, the lower than desired power efficiency of a conventional thermoelectric systems has hindered their widespread utilization and commercial deployment [1–3]. The future growth in the commercial applications of thermoelectric systems and their wider market penetration are primarily contingent upon increasing the power efficiency of these systems beyond their current levels.

The power efficiency of a typical thermoelectric device is strictly related to a dimensionless parameter called figure of merit, ZT, which is given as $ZT = S^2 \sigma T/K$. As seen from the aforementioned expression, the ZT value is directly influenced by the Seebeck coefficient S, the electrical conductivity σ, the absolute temperature in Kelvin T, and the thermal conductivity K [4–6].

Thermoelectric devices, in order to become competitive with conventional power sources and vapor-compression refrigerators, in terms of their energy efficiency, must be constructed with materials whose ZT values approach 4 [7]. Recent developments in the synthesis of both bulk and low-dimensional thermoelectric materials and advances in device fabrication have resulted in significantly improved thermoelectric figures of merit [8]. Thermoelectric thin films constitute one of the major and more

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promising low-dimensional thermoelectric material classes for advancing the state-of-art. The significance of thermoelectric thin films stems from several desirable aspects, including, their stronger quantum-confinement characteristic compared with that of their bulk material counterparts, a potentially more favorable carrier scattering mechanism, and a much lower lattice thermal conductivity [9].

SiGe alloys are widely known bulk materials for high-temperature power generation applications. Many researchers are working on SiGe and Si/Si + Ge multilayer thin film systems to reach higher thermoelectric efficiency [10–13]. ZT values can be tailored by increasing the cross plane Seebeck coefficient S and the cross plane electrical conductivity σ, and concurrently reducing the cross plane thermal conductivity K by bombarding the structure with MeV Si ion.

In previous studies we have investigated methods for the improvement of thermoelectric properties of thin film systems comprised of 100 and 50 nm multilayers as reported in Refs. [14,15]. We have also explored the positive effects, as they relate to higher figures or merit, of surface modification of Si/Ge multilayers by MeV Si ion bombardment and the results have been reported in Ref. [16]. We have achieved promising results related to the thermoelectric properties of Si–Ge systems and have demonstrated TEG systems with fairly high figures of merit as previously reported in Refs. [14–16]. We have also studied the high energy ion beam effects on the thermoelectric properties of 100 alternating layers of $SiO_2/SiO_2 + Ge$ multilayer thin film systems and have reached very high efficiency values at room temperature [17]. Our research group has also published the preliminary results pertaining to the current investigation of Si/Si + Ge multi-nanolayered superlattice films as reported in Ref. [18].

Following our initial success in the attainment of notably higher figures of merit in the preliminary studies conducted on Si/Si + Ge multi-nanolayered thin films, we focused our efforts toward continuing the thermoelectric characterizations at higher fluences of the MeV Si ion bombardment. In the current investigation, in addition to the standard characterization of thermoelectric properties of the multi-nanolayered thin films, we have also studied the optical properties of the Si/Si + Ge multilayer thin film systems using the optical absorption spectroscopy. This additional investigation was carried out in order to more accurately quantify the quantum dots and/or quantum cluster effects on the light absorptions. Raman Spectrometer was utilized to provide improved analysis of the multilayer films for a better understanding of the system order and the mutual bonds among the introduced elements in the multilayer systems.

In this paper, we report new experimental results related to the growth and characterization of two different groups of Si/Si + Ge multilayer superlattice film thermoelectric systems. The multilayer superlattice films were fabricated utilizing ion beam assisted deposition (IBAD), and were subsequently subjected to high energy Si ion bombardment. Ion beam bombardment is carried out in order to reduce thermal conductivity and increase electrical conductivity and Seebeck coefficient. Rutherford Backscattering Spectrometry (RBS), the optical absorption measurements were conducted in order to assess the effect of the variation of the fluences of the 5 MeV Si ion beam bombardment on the Raman Spectra.

2. Sample preparation and characterization

Fig. 1 shows the film geometry used for performing the cross plane electrical conductivity and the cross plane Seebeck measurements. Two classes of thermoelectric (TE) devices comprised of 50 and 100 alternating layers of Si/Si + Ge multilayer thin films were fabricated at the AAMU-Center for Irradiation of Materials (CIM).
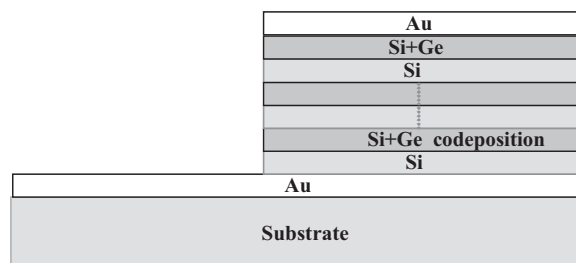

Fig. 1. Film geometry for the cross plane electrical conductivity and the cross plane Seebeck coefficient measurements.

These thin film formations constitute periodic quantum-well structures consisting of 50 and 100 alternating layers of Si and Si + Ge at total thickness of 300 and 317 nm, respectively. The multilayers were prepared by ion beam assisted deposition (IBAD) with rotating substrate holder during the deposition. The process pressure of the vacuum chamber of 5×10^{-6} Torr was maintained virtually constant throughout the deposition period with the careful considerations of all the experiment conditions. The multilayer films were sequentially deposited on Si and fused silica (suprasil) substrates with two metal (Au) contact layers at the top and bottom of the multilayer thin films in order to facilitate the cross plane electrical and the cross plane Seebeck coefficient measurements.

A quartz crystal monitor (QCM) was used to check the deposition rate and the final thickness of the multilayer Si/Si + Ge thin film structure. For each Si layer, the relative rate of deposition was 10 Hz/s from a single electron beam (e-beam) evaporator. Following the multilayer formation, the 5 MeV Si ion beam bombardment process was performed using the AAMU-CIM Pelletron accelerator in order to form nano (quantum) dots and/or nano-clusters in the layers. Stopping Range Ions in Matter simulation (SRIM) shows that 5 MeV Si ions pass through the multilayer thin films and terminate deep in the substrate.

The cross plane electrical conductivity was measured by the 4 probe-contact system. The cross plane thermal conductivity was measured by the home-made 3ω technique (3rd harmonic method). The cross plane Seebeck coefficient was measured by the MMR Technologies Seebeck measurement system. The cross plane electrical conductivity, the cross plane thermal conductivity and the cross plane Seebeck coefficient measurements were all performed at the room temperature. The experimental set-up and detailed information for 3ω technique can be found in Refs. [14,19,20].

In addition to the virgin case of the Si/Si + Ge multilayer thin film system, five different fluences were used for the 5 MeV Si ion bombardment at the fluence range of between 1×10^{12} ions/cm² and 1×10^{14} ions/cm². Rutherford Backscattering Spectrometry (RBS) was performed using 2.1 MeV He⁺ ions with the particle detector placed at 170° from the incident beam to monitor the quantitative amount of used elements in the thin film systems [21]. The prepared thin films were analyzed by Raman Spectrometry to detect nanoclustering in the multilayer films.

## 3. Results and discussions

We obtained negative values for the cross plane Seebeck coefficients for the Si/Si + Ge multilayer thin film systems. The measured negative value of the Seebeck coefficient indicates that our samples behave similar to n-type semiconductor materials. The measurements indicate that the 5 MeV Si ion beam bombardment at different fluence levels results in substantial improvement of the cross plane Seebeck coefficients of the thin film systems. For example, the thermoelectric device with 100 alternating layers of Si/Si + Ge multilayer thin film has Seebeck
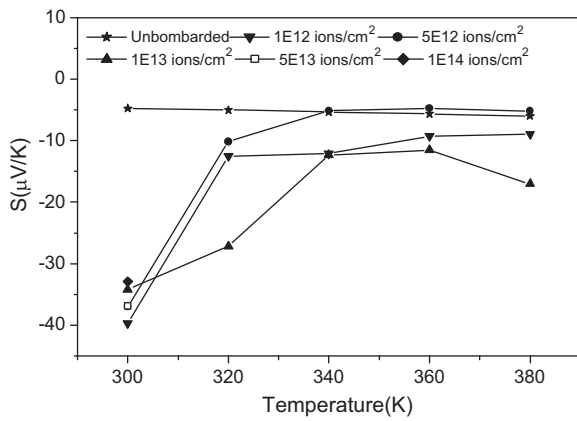
Fig. 2. Seebeck coefficient temperature dependence of the thin films with 50 alternating Si/Si + Ge multilayer films at different fluences.

coefficient of $-53.31\,\mu V/K$ at the virgin state (unbombarded); $-42.37\,\mu V/K$ at the fluence of 1×10^{12} ions/cm^2; $-82.87\,\mu V/K$ at the fluence of 5×10^{12} ions/cm^2; $-105.63\,\mu V/K$ at the fluence of 1×10^{13} ions/cm^2; $-44.08\,\mu V/K$ at the fluence of 5×10^{13} ions/cm^2; and $-61.18\,\mu V/K$ at the fluence of 1×10^{14} ions/cm^2. The increase in the absolute value of the cross plane Seebeck coefficient leads to more efficient thermoelectric materials and devices. Similar effects were observed in the multilayer thin film structure with 50 alternating Si/Si + Ge layers. Fig. 2 shows the Seebeck coefficient temperature dependence of Si/Si + Ge multilayer thin films at different fluence levels between 1×10^{12} ions/cm^2 and 1×10^{14} ions/cm^2 for a 50-layer structure. The Seebeck coefficient increased when the fluences were introduced at room temperature at all fluences. The virgin state multilayer film has the Seebeck coefficient of $-4.77\,\mu V/K$ at room temperature, whereas the Seebeck coefficient reached the maximum value of $-39.69\,\mu V/K$ at 1×10^{12} ions/cm^2 fluence at the same temperature. For the fluence levels tested, the Seebeck coefficients of the bombarded multilayers increased 8–9 times greater than the Seebeck coefficient of the corresponding virgin state (unbombarded) multilayers. Previously, we had investigated similar systems at different fluences and thicknesses and the results are reported in Ref. [15].

Fig. 3 shows the He RBS spectrum of the multilayer thin film with 100 alternating Si/Si + Ge layers prepared on Glassy Polymeric Carbon (GPC) substrate. We have used GPC for RBS measurement
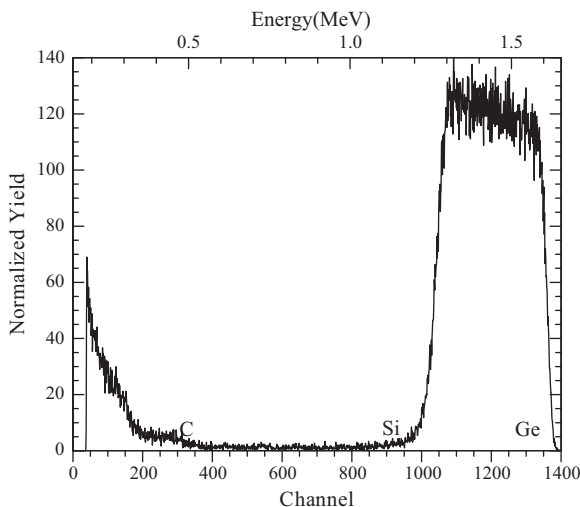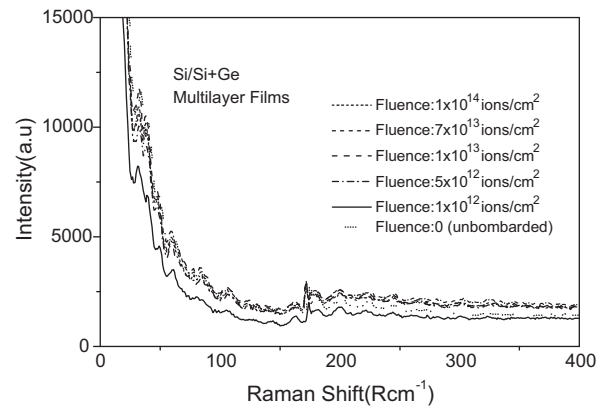
since carbon is lighter with respect to many other elements and it is easier to distinguish the used elements on the RBS measurement by using GPC substrate. In our future studies, we are planning to examine the detailed RBS and RUMP works for the Si/Si + Ge thin film systems which will be prepared using MBE and DC/RF sputtering depositions in order to improve the reproducibility of the higher efficiency thin film systems. We are planning to conduct RBS and RUMP studies on the future Si/Si + Ge thin films before and after the high energy Si ion beam bombardment is introduced at different fluences.

Fig. 4 shows the Raman Analysis of 50 alternating Si/Si + Ge amorphous multilayer films at different fluences. Dilor-JOBIN YVON-SPEX Raman Spectrometer was used to analyze the multilayer films for the order of the system and the bonds among the introduced elements in the multilayer thin film systems. The Raman spectrum of amorphous SiGe consists of three broad bands corresponding to the modes of Ge $\pm$ Ge, Si $\pm$ Ge and Si $\pm$ Si bonds, respectively [22]. The amorphous Ge–Ge bands lie between 200 and 300 cm^{-1}. The Si–Ge begins at 300 and ends at 400 cm^{-1}. We see continuous decrease in the intensity of the peaks in these regions as function of ion fluence. The higher fluence contributes more to the increased level of the damaged layers in the multilayer structure. We have defined peaks suggesting a Ge–Ge contribution from 180 to 300 cm^{-1} for the polycrystalline layers. In addition, the intensity of peaks in these regions decrease as a function of ion fluence suggesting that high fluence levels tend make the SiGe layers more amorphous.

Fig. 5 shows the thermoelectric properties of the 50 and 100 alternating Si/Si + Ge multilayer thin film systems. The square of the Seebeck coefficients of the 50 and 100 alternating multilayer thin films before and after 5 MeV Si ion bombardments at the five prescribed fluences at room temperature are compared in Fig. 5a and e, respectively. As seen from Fig. 5a and e, the squares of the Seebeck coefficients show both increasing and decreasing trends depending on the chosen fluences. Our expectation of increasing trends in Seebeck coefficients with higher fluences is, in principle, partially met. Although the experimental results do not completely bare out the prospect of higher Seebeck coefficient with increasing fluence, the trends confirm the general tendency. The Seebeck coefficient reaches substantially higher values for the 100 alternating layer thin film systems than the systems with 50 alternating layers.

The electrical conductivities of Si/Si + Ge multilayer thin films with 50 and 100 alternating layers before and after bombardment by the 5 MeV Si ions are shown in Fig. 5b and f, respectively. We used a digital electronic bridge with four-probe contact system by Agilent to measure the cross plane electrical conductivity of the thin film devices. It was assumed that the Schottky junction
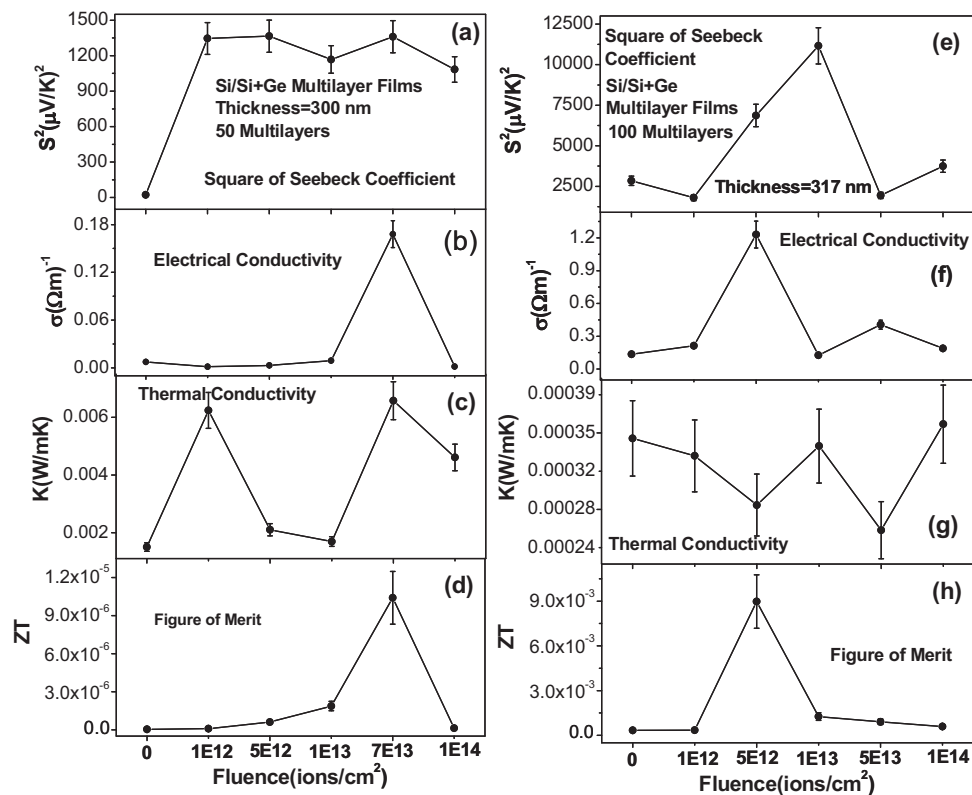

Fig. 4. Raman analysis of the thin films with 50 alternating Si/Si + Ge multilayer films at different fluences.

Fig. 3. He RBS spectrum of the thin films with 100 alternating Si/Si + Ge multilayer film on GPC substrate.

Fig. 5. Thermoelectric properties of the thin films with 50 and 100 alternating Si/Si + Ge multilayer thin film systems.

barrier between Au and the semiconductors and the resistance of the Au surface electrodes are negligible. As seen from Fig. 5b and f, the electrical conductivity values initially increased for lower fluences and decreased as fluence levels went up. The electrical conductivity reaches substantially higher values in the multilayers with 100 alternating layers of Si/Si + Ge thin films than the multilayers with 50 alternating layers of Si/Si + Ge, similar to the observed trends in the Seebeck coefficients. The cause of this phenomenon may be attributed to better layer homogeneity. The system with 100 alternating layers of Si/Si + Ge is comprised of layers which are substantially thinner than those of the system with 50 alternating layers of Si/Si + Ge, and thinner layers tend to be more homogeneous The expectation of increasing electrical conductivity with elevated fluence levels of the high energy ion beam are partially borne out by the experimental results.

The thermal conductivity values, in general, decrease with increasing ion fluence except for a few fluences for both 50 and 100 alternating layers of Si/Si + Ge multilayer thin films as seen from Fig. 5c and g. The multilayer thin films with 100 alternating layers reach substantially lower thermal conductivity values in comparison to the multilayer thin films with 50 alternating layers. This effect may be caused by thinner and therefore more homogeneous layers of the 100-layer system as discussed previously.

It is seen from the data of Fig. 5 that mutltilayer systems with more homogeneous and thinner layers, in general, lead to higher Seebeck coefficients and electrical conductivity, and lower thermal conductivity, provided they possess the optimal quantum stuructures (dots and/or cluster), which are formed at the suitable ion beam fluence levels.

Finally, we have calculated the figure of merit ZT from the definition $ZT = S^2\sigma T/K$ before and after bombardment by 5 MeV Si ions for the multilayer thin films with 50 and 100 alternating layers. The results for the figure of merit are given in Fig. 5d and h. Generally, the figure of merit tends to increase, for the multilayer thin films

with 50 and 100 alternating layers, as the fluence levels go up. This general trend, however, is violated at a few fluence levels, which may be attributed to defects caused by the bombardment. Based on our measured results, we have seen much more desirable effects in Seebeck coefficient as well as electrical and thermal conductivities for the multilayer thin films with 100 alternating layers as compared to the multilayer thin films with 50 alternating layers. We have achieved higher figure of merit values for the multilayer thin films with 100 alternating layers than the multilayer thin films with 50 alternating layers.

Our experimental data related to the multilayer thin film thermoelectrical characterizations show few anomalies, which are not supported by currently prevalent theory, at certain fluence levels of the high energy ion beam. We are planning to conduct more detailed investigations and carry out exhaustive measurement campaigns in the future to better assess the effects of fluence levels on the behavior of the thermoelectric system The planned investigations will provide a more robust theoretical underpinning and a more extensive experimental knowledge base for future thermoelectric studies. It will provide a better understanding of the effects of the ion beam bombardment and quantum dots/cluster formations on operation characteristics of the fabricated devices. We are also planning to carry out formal investigations with regards to the reproducabality of experimental results.

4. Conclusion

Bombardment of the multilayer system with the 5 MeV Si ion beam induces the formation of quantum dots and/or clusters of Si and Ge in the thin film systems. In addition to the quantum well confinement of phonon transmission due to Bragg reflection at lattice interfaces [23], the defects and disorder in the lattice caused by the bombardment process and the grain boundaries of these nanoscale clusters increase phonon scattering and increase the

chance of inelastic interactions and phonon annihilation. Thus, the cross plane thermal conductivity will decrease. These quantum dot multilayers also increase the cross plane Seebeck coefficient and the cross plane electric conductivity owing to the resultant higher electronic density of states produced by the one-dimensional periodic potential. The reduction in thermal conductivity may be attributed to both the multilayer interface and 5 MeV Si ion bombardment. The 5 MeV Si ion bombardment also increased the number of charge carriers in the multilayer films. This effect causes the electrical conductivity and the Seebeck coefficient to rise. We are planning to conduct more comprehensive investigations of the thermoelectric properties of thin film systems similar to the ones considered here. The future investigations will include more thorough measurement campaigns with finer adjustments of the ion beam fluences. It is anticipated that our planned experiments will further the state of knowledge beyond what is provided in this paper, and will offer quantitative guidelines with regards to the effects of ion beam bombardment on the performance characteristics of high efficiency thermoelectric devices.

Acknowledgements

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